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Free volume dilatation in polymers by ortho-positronium

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The possibility of positronium induced free volume cavity expansion in some polymers above the glass transition temperature was investigated using experimental positron annihilation lifetime data from the literature for polydimethylsiloxane, polyisobutylene, and polybutadiene as function of temperature. The results suggest that free volume sites can expand towards an equilibrium size, determined as the equilibrium Ps-bubble size defined earlier for low-molecular-weight liquids. The expansion can be explained by the increase of molecular mobility and hence decrease of relaxation times, which at the higher temperatures approach the o-Ps lifetimes. Nanoscale viscosities were estimated using Navier-Stokes equation and were found to be several orders of magnitude lower than the macroscopic viscosity at the same temperature. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4729561]

I. INTRODUCTION

During the last decades positron annihilation lifetime spectroscopy (PALS) has become an important tool when studying nanoscopic properties of polymers, molecular solids and liquids.[1,2] Positrons injected into polymers, molecular solids and liquids may form ortho-positronium (o-Ps) with an electron of parallel spin. The o-Ps probes the low electron density regions before annihilation. A simple relationship has been established by which the size of a free volume cavity can be estimated from the value of a measured o-Ps lifetime.[3,4]

For molecular liquids, it has been generally accepted that after o-Ps has been formed, a cavity develops (a so-called Ps-bubble), in which the o-Ps atom is localized. The bubble formation is a result of the repulsion between the molecules and the Ps atom (arising mainly from exchange interaction between the Ps electron and the molecular electrons).[1,3,5] The size of the bubble is determined by the balance between the outward pressure by the Ps zero-point motion and the inward pressure from the surface tension of the liquid (and the external pressure which is normally small in this connection).

For polymers, on the other hand, it has been assumed in many studies that the free volume hole sizes determined by PALS were intrinsic properties of the polymer under study and that the Ps probe did not perturb the free volume hole in which it was localized.[6–9] Schmidt *et al.*[8,10] observed a direct correlation between free volume fraction and free volume cavity size for a number of pressure densified polymer glasses, indicating the size of the free volume cavities to be a controlling factor for the temperature dependence of the specific volume. Dlubek *et al.* obtained similar results.[11–13]

For some polymers (and some glass-forming liquids) – when measured over a sufficiently wide temperature range – it has been observed that the o-Ps lifetime as a function of temperature exhibits at least two major changes of slope.[14–22] A major increase of slope at low temperatures reflects the transition of the polymer from a glassy to a rubbery state (at the glass transition temperature T_g) and is accompanied by an increase of the expansion coefficient of the macroscopic volume. At temperatures above approximately 1.2–1.6 × T_g, a clear decrease in slope may be observed. However, this decrease in slope is not reflected in the expansion of the macroscopic volume.[13] At such relatively high temperatures, polymers are characterized by short segmental relaxation times of the same order of magnitude as the o-Ps lifetimes.[23] At these temperatures, o-Ps can therefore be considered to experience a dynamic environment, which has been recognized by several authors.[13,15,20]

The leveling off of the o-Ps lifetime at the highest temperatures has been a subject of considerable debate.[1,6,12,17,24–26] One suggestion has been that the leveling off is due to the increased amplitude of the molecular fluctuations, which results in an increased average overlap of the o-Ps with the electrons of the surrounding molecules and hence counteracts the effect of increasing free volume sizes with temperature. Another suggestion has been that the leveling off is due to the formation of equilibrium 'Ps bubbles', similar to Ps-bubbles in ordinary liquids. In the present paper, we shall discuss results that seem to support the latter view.

II. EQUILIBRIUM BUBBLE SIZE AND MACROSCOPIC SURFACE TENSION

As mentioned above, for a large number of molecular liquids, the Ps-bubble size and hence the o-Ps lifetime, $\tau_{o\text{-}Ps}$, is determined by the balance between the zero-point pressure of o-Ps and the contractive forces of the liquid, i.e., the surface tension. Several authors have demonstrated and discussed this correlation between $\tau_{o\text{-}Ps}$ and surface tension.[2,3,27–29] A simple, approximate correlation has been established, as given by

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Eq. (1) with typical values for c and d in the ranges of 0.046–0.061 and 0.50–0.55, respectively, with the surface tension in dyne/cm (10^{-3}N/m) and the o-Ps lifetime in ns,

$$\tau_{o-Ps}^{-1} = c\gamma_{macro}^{d}. \quad (1)$$

Recently, Winberg *et al.*[19] reported that the o-Ps lifetime in the polymer polydimethylsiloxane (PDMS) measured at temperatures above 1.6 × T_g was related to the macroscopic surface tension and could be well fitted by Eq. (2),

$$\tau_{o-Ps}(T) = 0.15 + 0.058^{-1}\gamma^{-0.5}(T). \quad (2)$$

This relation is very similar to Eq. (1) and was therefore taken to suggest that free volume sites might have been expanded into equilibrium o-Ps bubbles in PDMS above 1.6 × T_g.

In order to investigate this suggestion further, we extend in the present contribution the range of lifetimes and corresponding surface tensions by including experimental results for two other polymers, polyisobutylene (PIB) and polybutadiene (PB), with different glass transition temperatures.

III. EXPERIMENTAL

In the present work, we have taken data from the literature[19,21] for o-Ps lifetimes measured as functions of temperature for three different polymers. All sets of data were recorded at the (then) Risoe National Laboratory. One polymer was Vinyl-terminated PDMS with a number average molecular weight of 155 000 g/mol,[19] the other material was PIB with a molecular weight of 850 000 g/mol[21] and the third material was PB with a molecular weight of 810 000 g/mol.[21] All three sets of measurements were carried out in a wide temperature range (80 K to 373 K for PDMS, 80 K to 460 K for PIB and 80 K to 350 K for PB), i.e., from well below the glass transition temperature T_g to well above the "leveling off" temperature (knee temperature) T_k of about 1.6 × T_g. The specimens had been kept under vacuum during the measurements, which were carried out with a conventional fast-fast lifetime spectrometer with a time resolution of FWHM ≈260 ps. A total of at least 1.5 × 10^6 counts had been recorded in each spectrum. The lifetime spectra were decomposed into three lifetime components by using the least squares fitting program PATFIT.[30] In the present work, we discuss the lifetime τ_3 of the most long-lived component which is due to pick-off annihilation of o-Ps.

IV. EXPERIMENTAL DATA

Figure 1 depicts o-Ps lifetimes ($\tau_{o\text{-}Ps}$) versus macroscopic surface tensions (γ) for PDMS, PIB and PB. For each polymer, increasing temperature corresponds to decreasing surface tension. Data for the temperature dependent macroscopic surface tensions were extracted from Brandrup *et al.*[31] Arrows indicate glass transition temperatures (T_g) and knee temperatures (T_k). The two solid thin curves represent the semi-empirical relation Eq. (1) by Tao[3] for the parameters c and d equal to 0.061, 0.5, and 0.046, 0.55, respectively, while the brown dotted curve is a fit to the points for the three polymers above their respective knee temperatures (T > T_k). The dotted curve is given by $\tau_{o\text{-}Ps} = 0.32 + 0.062^{-1}\gamma^{-0.5}$, i.e., fairly close to Eqs. (1) and (2).

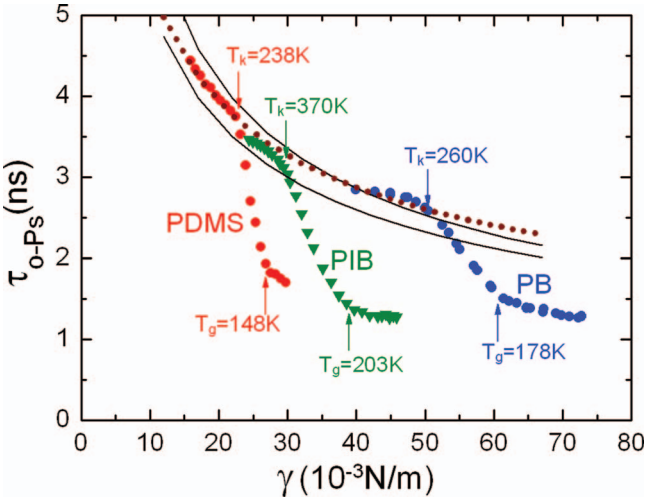

FIG. 1. Correlation between macroscopic surface tension (γ) and o-Ps lifetime ($\tau_{o\text{-}Ps}$) for PDMS (Ref. 19), PIB (Ref. 21), and PB (Ref. 21). The dotted brown curve is a fit to the points for the three polymers above their respective knee temperatures (T > T_k). Glass transition temperatures (T_g) are indicated. So are the 'knee' temperatures (T_k) above which o-Ps bubbles appear to be formed. The two thin black curves define the range of values for the $\tau_{o\text{-}Ps}$ vs. γ correlation observed for molecular liquids by Tao (Ref. 3) (Eq. (1)).

Figure 1 exhibits two striking features of the lifetime data – when plotted as function of surface tension. One feature is that for surface tensions lower than those at the glass transitions, each polymer shows a steep rise of the o-Ps lifetime with decreasing surface tension. The second feature is the sharp change in slope when the lifetime reaches values within or close to the range defined by Eq. (1). Furthermore, for these low values of the surface tensions (i.e., at temperatures above T_k) the lifetimes correlate very well with γ in the same manner as has been observed for molecular liquids.[3] This correlation between surface tension and lifetime is a strong indication that at temperatures above T_k, o-Ps exists in an equilibrium bubble state and the lifetime is no longer a measure of the free volume cavity size, but rather of the equilibrium o-Ps bubble size (R_{bubble}).

Considering that polymer segmental relaxation times at these temperatures (T ≥ T_k) are of the same order of magnitude, or shorter than the o-Ps lifetime, it is not difficult to accept that the relatively high pressure of o-Ps in a free volume cavity could expand this cavity within the o-Ps lifetime. In the light of these considerations, it is important to explore the circumstances under which o-Ps interacts with its dynamic polymer environment and how the free volume site expands.

V. THEORETICAL CONSIDERATIONS

A. Equilibrium bubble size

A simple model of the Ps bubble state in a liquid assumes that Ps is localized in an infinitely deep spherical potential well with a radius R.[1,2] The total energy of the Ps bubble can be written as Eq. (3a) and (3b) where E_0 is the zero-point energy of Ps, γ the surface tension of the liquid and P_{ext} the

external pressure (which can often be assumed negligible under atmospheric conditions). The Ps bubble is in equilibrium (with a radius R_{eq}) when the total energy is minimum. In Eq. (3b), $\hbar$ is the reduced Planck's constant and m the electron mass,

$$E_{tot} = E_0 + 4\pi R^2\gamma + \tfrac{4\pi R^3}{3} P_{ext}, \tag{3a}$$

where

$$E_0 = \frac{\pi^2\hbar^2}{4mR^2}. \tag{3b}$$

Due to the rather extreme curvature of the surface of a positronium bubble it is reasonable to assume that the valid surface tension in Eq. (3a), will deviate from the macroscopic surface tension.[32,33] We refer to that as the nanoscopic surface tension, γ_{nano}.

The relationship between lifetime and cavity radius has often been approximated by Eq. (4a).[3,4] Here R_0 is the radius of an infinite spherical potential well, covered by an electron layer with a thickness δ (= R_0-R) of 0.166 nm,

$$\tau_{o-Ps} = 0.5\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\frac{2\pi R}{R_0}\right)^{-1}. \tag{4a}$$

$$V_{o-Ps} = \frac{4\pi R^3}{3}. \tag{4b}$$

We should emphasize that the above equations (3) and (4) are simplified formulas. Various authors[2,27–29,33,34] have derived more detailed descriptions of the above relationships, in particular trying to take into account that the localization potential for Ps has a final depth and is not necessarily of spherical shape, or that Ps is not a point particle, but a two-particle bound state. However, for the present purpose Eqs. (3) and (4) will suffice. For example, Eq. (4) has been calibrated using a number of molecular solids and zeolites and has been generally applied to o-Ps lifetimes in polymers. It should also be mentioned that the radius R reflects a characteristic length scale representing a distribution of cavity sizes of different shapes.

B. Free volume cavity expansion

As suggested above, a free volume cavity (of radius R_{FV}) in which a positronium atom is localized may be expanded to an equilibrium bubble (of radius R_{bubble}), as a result of the zero-point pressure of positronium. Resistance to growth is caused by contractive stresses by the surface tension and viscous friction of the flow of material. This is schematically illustrated in Fig. 2.

Assuming constant density, spherical symmetry and Newtonian behavior of the surrounding polymer liquid the growth process can be described in terms of the Navier-Stokes equation,[35,36]

$$P_{o-Ps} - P_\gamma = \frac{4\eta_{o-Ps}}{R}\frac{dR}{dt}, \tag{5}$$

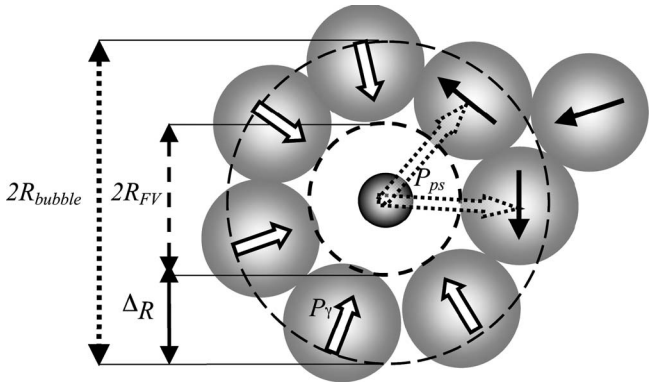

FIG. 2. Simple, schematic illustration of the expansion of a free volume cavity. In this simple 2-dimensional sketch of the 3-dimensional structure of cavity and molecules, the light grey circles (spheres) represent monomers or segments of the polymer chains, while the small, darker circle represents the Ps atom localized in the cavity. The cavity may expand from the size of a free volume cavity (of radius R_{FV}) to the equilibrium bubble (of radius R_{bubble}), as a result of the Ps outward pressure (P_{Ps} – dotted arrows). The pressure due to the surface tension (P_γ – empty arrows) counteracts expansion. Filled arrows indicate direction of moving molecular segments between which viscous friction occurs, causing dissipation of energy.

where the zero-point pressure by o-Ps, $P_{o\text{-}Ps}$, and the pressure by the surface tension, P_γ, are given by

$$P_{o-Ps} = \frac{dE_0}{dV} = \frac{\pi\hbar^2}{8mR^5} \tag{6a}$$

and

$$P_\gamma = \frac{d(4\pi R^2\gamma)}{dV} = \frac{2\gamma}{R}, \tag{6b}$$

and $\eta_{o\text{-}Ps}$ in Eq. (5) constitutes a Newtonian shear viscosity (which equals $\eta_{ex}/3$ where η_{ex} is the extensional viscosity).[37,38]

The solutions of Eqs. (5) and (6) are based on continuum mechanics principles. However, as an approximation we will apply these relations on the nanoscale problem of Ps-bubble expansion, defining R by the o-Ps lifetime (Eq. (4a)). Expansion of free volume cavities is then governed by the nanoscopic extensional viscosity η_{ex}.

In order to make a comparison of experimental data with the simple picture of bubble expansion outlined above (Eqs. (5) and (6)) and Fig. 2), we have chosen to plot in Fig. 3 the average cavity size in PIB as detected by o-Ps (using Eqs. (4)) as a function of temperature.

In accordance with Fig. 1, we assume that at high temperatures (T > ~370 K), equilibrium Ps bubbles (of volume $V_{equilibrium}$) are formed. Further we expect that at lower temperatures equilibrium bubbles will not be able to form because the polymer segmental relaxation times are too long compared to the o-Ps lifetime, $\tau_{o\text{-}Ps}$. If equilibrium bubbles had been able to form, their size would have decreased somewhat with decreasing temperature, as indicated by the bold dotted brown curve ($V_{equilibrium}$) in Fig. 3, due to the increasing surface tension at lower temperatures.

At low temperatures, below and somewhat above the glass transition temperature T_g, the polymer segmental relaxation times are generally in the range of ~1 – 100 s, i.e., considerably longer than the o-Ps lifetime, $\tau_{o\text{-}Ps}$.

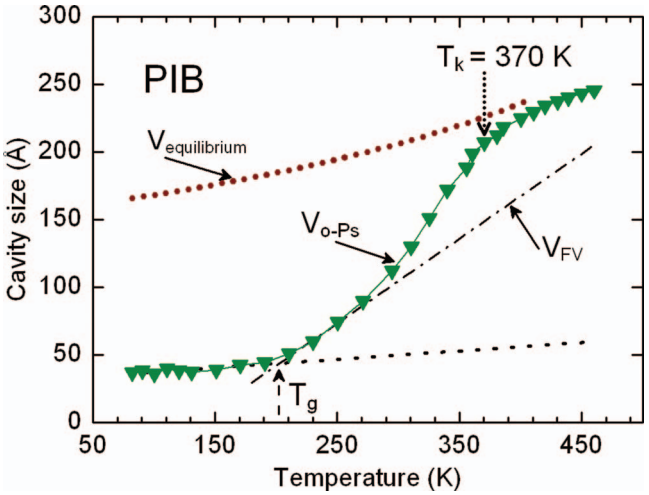

FIG. 3. Cavity sizes $V_{o\text{-}Ps}$ (green triangles) in poly(isobutylene) derived from o-Ps lifetimes measured by Zrubcova *et al.* (Ref. 21) in the temperature range between 80 and 460 K using Eqs. (4). The dash-dotted line marked V_{FV} shows free volume cavity sizes linearly extrapolated (Eq. (7)) from values in the range $T_g < T < 270$ K. The brown dotted curve identified as $V_{equilibrium}$ shows the hypothetical equilibrium bubble size in the whole temperature range, as derived from the dotted curve in Fig. 1. The glass transition temperature (T_g) and knee temperature (T_k) are indicated. The latter is associated with the onset of equilibrium o-Ps bubbles.

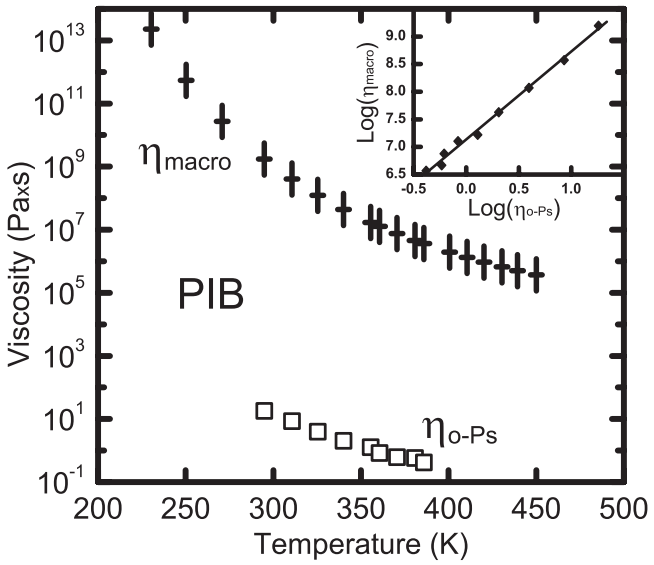

FIG. 4. Comparison of macroscopic (†, η_{macro}) and estimated nanoscopic viscosity (□, $\eta_{o\text{-}Ps}$) of PIB. The macroscopic viscosity was calculated from a relation by Fox and Flory (Ref. 40). The lengths of the vertical bars used as symbols mark the variation of the calculated viscosity for different molecular weights (Ref. 41). The nanoscopic viscosity was estimated using the Navier-Stokes equation (see text). Inserted in top right corner is a log-log plot of the estimated correlation between η_{macro} and $\eta_{o\text{-}Ps}$ which has been approximated by a straight line (Eq. (8)).

Using the WLF-equation[39] as an approximation, it is possible to estimate the temperature range in which the segmental relaxation times are of the order of ~1 ns, i.e., the same order of magnitude as $\tau_{o\text{-}Ps}$. The estimated range of temperatures turns out to be 50–80 K above T_g. These temperatures fall in the range between T_g and T_k (Fig. 1).

Because of the very long relaxation times at temperatures around T_g, as mentioned above, we find it unlikely that Ps-bubbles can develop at these temperatures, and the cavity sizes detected by o-Ps will be the free volume cavity size of average radius R_{FV} and equivalent volume V_{FV} as indicated with the dotted line below T_g and the dash-dotted line for $T_g < T < \sim 270$ K in Fig. 3. Assuming a constant number of free volume cavities,[8,13] the free volume cavity size should approximately be represented by the linear extrapolation of V_{FV} to temperatures above 270 K, given by

$$V_{FV} = 0.7T - 102, \tag{7}$$

where V_{FV} is in units of Å^3.

Clearly, at temperatures above ~270 K the linearly extrapolated V_{FV} does not agree with the observed cavity sizes, $V_{o\text{-}Ps}$ (Fig. 3). We assume that this deviation is due to expansion of the free volume cavities by the Ps zero-point pressure, $P_{o\text{-}Ps}$. Using Eq. (5) to approximately describe the expansion (from a radius of R_{FV} to $R_{o\text{-}Ps}$) to take place during a time interval equal to the lifetime of o-Ps ($\tau_{o\text{-}Ps}$) we can estimate the nanoscopic viscosity $\eta_{o\text{-}Ps}$ at the different temperatures. The results are shown in Fig. 4 where $\eta_{o\text{-}Ps}$ is also compared with the macroscopic viscosity (η_{macro}), which was calculated from a relation by Fox and Flory:[40,41] $\log(\eta) = 3.4 \times \log(M) + 5.6 \times 10^5/T^2 - 16.85$. This relation is valid at temperatures between 233 and 490 K and for narrow molecular mass distributions with M >17000 g/mol.[41] The unit for viscosity is [Pa × s].

Fig. 4 shows that the estimated $\eta_{o\text{-}Ps}$ is several orders of magnitude lower than η_{macro}.

Due to the various approximations mentioned above there is some uncertainty associated with the estimates of $\eta_{o\text{-}Ps}$. However, this uncertainty cannot account for the huge difference between η_{macro} and $\eta_{o\text{-}Ps}$ shown in Fig. 4.

The possible difference between microscopic and macroscopic viscosity has been considered by Wyart and de Gennes.[42] They recognized that the microscopic viscosity cannot equal the macroscopic counterpart. The high viscosity of polymer melts arises from entanglement effects, caused by their long chain nature.[39] Wyart and de Gennes predicted that displacements involving only a small portion of the chain, typically smaller than 50 Å, would not put entanglements into play. In such a case, the microscopic viscosity should instead be described as $\eta_{micro} = \eta_{monomer} \times n_b$, where $\eta_{monomer}$ is the viscosity of an equivalent liquid of monomers and n_b is the number of monomers in the portion of the chain involved in the displacement. These considerations therefore seem relevant for Ps-bubble formation in polymers, since Ps bubble formation in polymers typically will result in radial displacements of cavity walls of only fractions of a nanometer. Hence, following Wyart and de Gennes, the nanoscopic viscosity experienced by o-Ps would be expected to be considerably smaller than the macroscopic viscosity.

The approximate relation between the two viscosities is shown in the insert in Fig. 4 and can be represented by a straight line,

$$\log(\eta_{macro}) = 1.6 \times \log(\eta_{o-Ps}) + 7.14. \tag{8}$$

Although Eq. (8) yields at best an approximate description of $\eta_{o\text{-}Ps}$, it may be used as an estimation of the relation

between macroscopic viscosity and $\eta_{o\text{-}Ps}$ also for other polymers. In order to estimate the free volume cavity expansion in for example PDMS at $T > T_g$ using the relation between macro and nanoscopic viscosity (Eq. (8)), the free volume sizes in PDMS at temperatures above T_g could in principle be predicted. However, such a prediction for rubbery PDMS appears to be more complicated and arbitrary than in the case of PIB. PDMS is a semi-crystalline polymer, which due to the flexible siloxane linkage in the backbone has a glass transition temperature of about 148 K. Liquid-like behavior with relaxation times on the order of nanoseconds is reached at about $T_g + 50$ K, which is less than for PIB. Hence, the temperature region where actual free volume sizes (V_{FV}) can be established ($\tau_{relax} \gg \tau_{o\text{-}Ps}$), is shorter in the case of PDMS than for PIB.

VI. CONCLUSIONS

The present paper has attempted to set up a simple model that can rationalize the characteristic variation of the o-Ps lifetime with temperature that has been observed in positron lifetime measurements for several polymers. In the low-temperature, glassy state of a polymer the o-Ps lifetime increases slowly with temperature. Above the glass transition temperature (T_g) the increase is more rapid, while at the highest temperatures (above a certain "knee temperature" T_k) the o-Ps lifetime again levels off.

Using data for three well characterized polymers (PIB, PDMS and PB) we point out that in the temperature region above T_k the lifetimes – when plotted as functions of surface tension – quantitatively follow a relationship found by Tao[3] for a large number of ordinary liquids and ascribed by him to the formation of equilibrium Ps bubbles in these liquids. We take this observation as a strong indication that the leveling off of o-Ps lifetimes above T_k is not due to a molecular transition or sudden change of intrinsic properties of the polymers, but rather to a local pertubation of the polymer structure by the Ps atom itself. Ps is localized in a free volume cavity, but the pertubation leads to an expansion of the cavity until an equilibrium state has been established (similar to Ps bubbles in ordinary molecular liquids). T_k may therefore approximately be the temperature at which the segmental relaxation time becomes of the same order of magnitude as the o-Ps lifetime.

It is furthermore suggested that for temperatures in the region between T_g and T_k a cavity in which Ps is localized will not be able to expand into an equilibrium state because the relaxation times of the polymer molecules are too long compared to the o-Ps lifetimes of a few ns. However non-equilibrium expanded cavities may develop at these temperatures, their sizes approaching that of equilibrium cavities as the temperature approaches T_k. As a consequence, the increase of the o-Ps lifetime between T_g and T_k not only reflects the thermal expansion of the intrinsic free volume of the polymer, but is also a result of an expansion of the free volume cavity in which the Ps atom is localized, the degree of expansion being larger at increasing temperatures of the polymer.

An approximate quantitative description was given of the above qualitative picture of cavity expansion, which led to estimates of viscosities that should be associated with nanometric sized cavities. These viscosity values are found to deviate appreciably from the equivalent quantities for bulk systems.

These findings, although at this point merely qualitative, encourage further studies of the expansion of free volume sites by the ortho-Positronium pressure and molecular dynamics and their possibilities to uniquely determine rheological data on a nano scale. Further studies will ensure accurate measurement of free volume sizes, appropriate relation to macroscopic properties and also provide further insight into some nanoscopic properties of polymers.

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